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A new relation to estimate adiabatic compressibility of binary mixtures at different temperatures and concentrations

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Abstract . Using the definition of adiabatic compressibility, a new relation has been deduced to estimate the adiabatic compressibility of liquid mixtures at different temperatures from the knowledge of temperature coefficients of sound velocity and density of pure components The validity of the relationship is examined by comparing the calculated values with the experimental values of adiabatic compressibility of three binary liquid mixtures, benzene + toluene, pyridine + water and polymethylmethacrylate + chlorobenzene at different temperatures and the results are explained on the basis of molecular interaction between the components

Keywords . Binary liquid mixtures, adiabatic compressibility, molecular interaction.

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1. Introduction

The ultrasonic technique, due to their simplicity and accuracy, is being most widely used in the study of liquid state, the most complicated among the three states of matter. We are engaged in a systematic study of liquid state using a few opto-acoustic properties of liquids [1-3]. In this paper, we are reporting the deduction of a new relation to estimate the adiabatic compressibility β_s of liquid mixtures at different temperatures from the knowledge of temperature coefficients of density ρ of pure components and sound velocity U in them. This relation is used to estimate β_s of three binary mixtures *viz.* benzene + toluene, pyridine + water and polymethylmethacrylate + chlorobenzene (PMMA + CB) at different temperatures. The estimated values are then compared with the experimental values for these systems.

2. Experimental details

The sound velocity and density have been determined experimentally for the binary systems pyridine + water and benzene + toluene. Chemicals of AR/BDH grade and distilled water were used for experimental purpose. The purity of these liquids were tested by comparing their densities with those in literature and found to be in good agreement. The ultrasonic velocities of these mixtures were measured using a single-crystal ultrasonic interferometer supplied by Mittal Enterprises at a frequency of 2MHz and the densities were determined by a 12 cm^3 double-stem pyknometer. The masses were recorded on an electronic balance having an accuracy of ± 0.1 mg. The experiments were carried out at different temperatures using a thermostatically controlled water circulating arrangement with an accuracy of ± 0.1 K. The data for calculating β_s of polymethylmethacrylate + chlorobenzene system were taken from literature [4].

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3. Theory

The adiabatic compressibility (β_s) is related to ρ and U through the relation

$$\beta_s = (U^2\rho)^{-1}. \quad (1)$$

As temperature of the liquid changes, the adiabatic compressibility also changes. Both U and ρ are temperature sensitive parameters. So differentiating eq. (1) with respect to temperature and dividing by β_s throughout, we get

$$(1/\beta_s)(\partial\beta_s/\partial T)_p = -(1/\rho)(\partial\rho/\partial T)_p - (2/U)(\partial U/\partial T)_p$$

$$= \alpha + 2\beta, \quad (2)$$

where $\alpha = -(1/\rho)(\partial\rho/\partial T)_p$ is the temperature coefficient of density

and $\beta = -(1/U)(\partial U/\partial T)_p$ is the temperature coefficient of sound velocity

From eq. (2)

$$d\beta_s/\beta_s = (\alpha + 2\beta)dT. \quad (3)$$

Integrating eq (3)

$$\ln\beta_s = (\alpha + 2\beta)T + C. \quad (4)$$

where C is a constant of integration

If β'_s is the adiabatic compressibility at another temperature $T'(T' < T)$, then from eq. (4)

$$\ln\beta'_s = (\alpha + 2\beta)T' + C \quad (5)$$

From eqs. (4) and (5), we get

$$\ln(\beta_s/\beta'_s) = (\alpha + 2\beta)(T - T')$$

or $$\beta_s = \beta'_s \exp(\alpha + 2\beta)\Delta T, \quad (6)$$

where $\Delta T = T - T'$.

This is the temperature dependent relation of adiabatic compressibility of a liquid.

If the adiabatic compressibility β'_s of a liquid mixture at a temperature T' is known, the adiabatic compressibility at a higher temperature T can be estimated using eq. (6) knowing the values of α and β. In the case of a binary mixture, α and β were taken as the mean of the component values $\alpha = (\alpha_1 + \alpha_2)/2$ and $\beta = (\beta_1 + \beta_2)/2$, where α_i and β_i are the temperature coefficients of density and sound velocity of i-th component.

4. Results and discussion

The calculated values of β_s using eq. (6) along with the experimental values for the binary systems benzene + toluene, pyridine + water and polymethyl methacrylate + chlorobenzene are presented in Table 1. The variations of β_s with molefraction of the first component (x_1) at different temperatures for the above mixtures are shown in Figures 1 to 3.

Figure 1 shows the variation of β_s^{Expt} and β_s^{cal} with molefractions for the binary mixture benzene (x_1) + toluene ($1-x_1$) at 313 and 323 K. We choose this system for our present study because it has been accepted as an ideal mixture [5]. The figure shows that the calculated values agree well with the experimental values within experimental error for the whole composition range at both temperatures. This indicates that the system acts as an ideal mixture having no molecular interaction which is in agreement with the accepted fact. It also exhibits that for a non-interacting system, the calculated values using the new relation agree well with the experimental values.

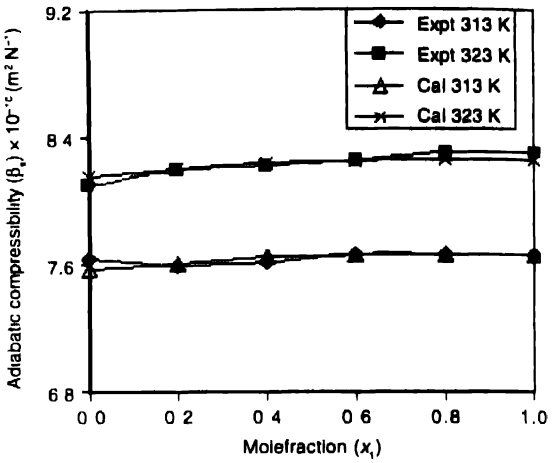

Figure 1. Variation of β_s^{Expt} and β_s^{cal} with molefraction (x_1) for the binary mixture benzene + toluene at 313 and 323 K

Figures 2 (a–c) show the variation of β_s with molefraction for the binary mixture pyridine (x_1) + water ($1-x_1$) at 303, 308 and 313 K respectively. As the shape of the curves using calculated values are similar to the experimental curves, the calculated values agree with the experimental values. At lower temperature, the theoretical curve deviates slightly from the experimental curve

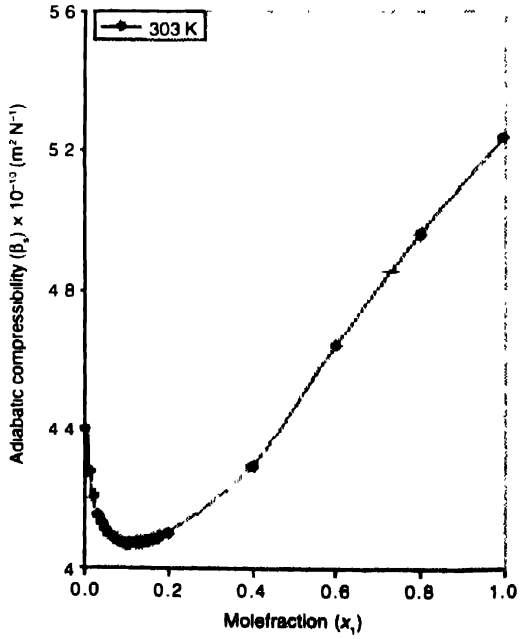

Figure 2(a). Variation of β_s^{Expt} with molefraction (x_1) for the binary mixture pyridine + water at 303K

Table 1 Variation of β_s^{Expt} and β_s^{cal} with concentration for different binary mixtures at different temperatures.

(a) **Benzene + Toluene**

x_1	U ms^{-1}			ρ kg m^{-3}			$\beta_s^{Expt} \times 10^{10}$ m^{2}N^{-1}			$\beta_s^{cal} \times 10^{10}$ m^{2}N^{-1}	
	303 K	313 K	323 K	303 K	313 K	323 K	303 K	313 K	323 K	313 K	323 K
0.00	1289	1248	1212	858.1	841.7	840.0	7.01	7.63	8.10	7.56	8.15
0.20	1285	1245	1205	858.8	850.0	840.4	7.05	7.59	8.19	7.60	8.20
0.40	1282	1243	1202	859.5	850.4	841.6	7.08	7.61	8.22	7.64	8.23
0.60	1280	1238	1199	860.6	852.0	842.9	7.09	7.66	8.25	7.65	8.25
0.80	1278	1237	1194	861.9	853.0	845.0	7.10	7.66	8.30	7.66	8.26
1.00	1275	1236	1193	866.1	855.6	846.2	7.10	7.65	8.30	7.66	8.26

(b) **Pyridine + Water**

	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K	308 K	313 K
0.00	1510.4	1520.7	1528.7	995.670	994.055	992.200	4.403	4.350	4.313	4.506	4.611
0.01	1531.1	1538.0	1544.5	996.102	994.192	992.200	4.282	4.252	4.225	4.382	4.484
0.02	1544.1	1548.7	1553.3	996.317	995.056	991.749	4.210	4.190	4.179	4.308	4.409
0.03	1552.5	1555.6	1556.4	997.749	995.115	992.475	4.158	4.153	4.159	4.255	4.354
0.04	1556.6	1559.0	1558.7	997.749	995.507	992.357	4.136	4.133	4.148	4.232	4.331
0.05	1560.5	1560.7	1559.9	997.533	995.899	992.435	4.117	4.122	4.141	4.213	4.311
0.06	1563.2	1562.7	1560.3	998.122	995.997	992.651	4.100	4.111	4.138	4.196	4.294
0.07	1564.7	1562.8	1559.5	998.612	996.194	992.357	4.090	4.110	4.143	4.185	4.283
0.08	1566.0	1562.9	1558.1	998.514	996.233	992.769	4.084	4.109	4.149	4.179	4.277
0.09	1567.7	1563.2	1558.2	998.279	995.978	991.710	4.076	4.109	4.153	4.171	4.268
0.10	1567.3	1562.3	1556.5	999.142	996.449	992.926	4.074	4.112	4.157	4.169	4.266
0.11	1566.9	1561.0	1554.6	999.181	996.625	992.220	4.076	4.118	4.170	4.171	4.268
0.12	1566.8	1560.4	1552.8	999.063	996.096	991.827	4.077	4.123	4.182	4.172	4.269
0.13	1566.9	1560.0	1552.0	999.122	995.899	991.710	4.077	4.126	4.186	4.172	4.269
0.14	1566.8	1558.5	1550.4	999.122	995.880	991.533	4.077	4.134	4.196	4.172	4.269
0.15	1566.1	1557.8	1548.4	999.142	995.625	991.533	4.081	4.139	4.207	4.176	4.274
0.16	1564.8	1556.2	1545.4	999.005	995.585	991.180	4.088	4.148	4.224	4.183	4.281
0.17	1564.7	1554.6	1544.3	998.848	995.703	990.612	4.089	4.156	4.233	4.184	4.282
0.18	1563.5	1553.6	1542.3	998.612	995.252	990.494	4.096	4.163	4.244	4.192	4.289
0.20	1561.9	1550.7	1539.1	998.651	995.173	991.122	4.105	4.179	4.259	4.201	4.299
0.40	1528.7	1512.6	1495.4	995.533	990.818	985.572	4.298	4.411	4.537	4.398	4.501
0.60	1475.9	1458.4	1441.5	987.844	984.009	978.200	4.647	4.778	4.920	4.755	4.866
0.80	1434.0	1415.4	1397.5	979.193	974.479	968.596	4.966	5.122	5.286	5.082	5.200
1.00	1400.1	1381.9	1362.6	973.348	968.646	962.650	5.241	5.406	5.595	5.363	5.488

(c) **Polymethylmethacrylate + Chlorobenzene**

	303 K	313 K	323 K	303 K	313 K	323 K	303 K	313 K	323 K	313 K	323 K
0.00	1251.0	1215.0	1179.0	1107.5	1104.04	1102.12	5.769	6.136	6.528	6.115	6.482
0.25	1251.0	1215.0	1179.0	1108.9	1106.12	1104.38	5.762	6.124	6.514	6.108	6.475
0.50	1252.0	1215.0	1181.0	1110.3	1108.29	1107.17	5.740	6.112	6.476	6.085	6.450
0.75	1252.0	1215.0	1181.0	1115.1	1109.92	1110.67	5.721	6.103	6.455	6.065	6.429
1.00	1253.0	1219.0	1184.0	1115.9	1113.92	1112.71	5.708	6.041	6.411	6.065	6.414
2.00	1254.0	1221.0	1190.0	1117.3	1115.89	1114.73	5.691	6.011	6.335	6.033	6.395
3.00	1257.0	1226.0	1201.0	1118.1	1116.10	1115.99	5.660	5.961	6.212	6.000	6.360

x_1 - Mole fraction

X - Wt. % of PMMA

As the temperature is increased, this deviation is also increased indicating the presence of molecular interaction in this system. Other studies at low concentration have established the fact that there is strong molecular interaction between the components of this system [6].

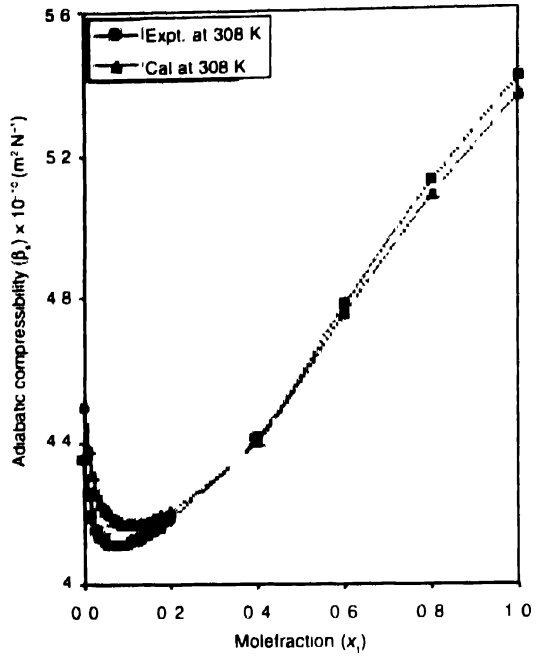

Figure 2(b). Variation of β_s^{Expt} and β_s^{cal} with molefraction (x_1) for the binary mixture pyridine + water at 308 K

Babu *et al* [6] studied pyridine water binary system at only one temperature *viz.*, 303 K and obtained a compressibility minimum at 0.13 molefraction of pyridine. They explained the minimum compressibility as the formation of pyridine-water complexes at low concentrations.

Water is a hydrogen bonding solvent and pyridine with lone pair of electron on N-atom is also capable of H-bonding with water molecules. A hydrogen bond is a very strong dipole attraction between a hydrogen attached to a strongly electronegative atom such as fluorine, oxygen, and nitrogen of a polar molecule [7]. In pyridine-water system, it is found that the excess values of β_s (β_s^E) are negative up to x_1 = 0.28 molefraction of pyridine and changes sign beyond this. The experimental curve crosses the theoretical curve at around x_1= 0.3 molefraction at 308 K and at higher temperature 313 K, this point shifts to lower concentration. This is the point where β_s^E changes sign from negative to positive. It has been reported that the negative value of β_s^E is an indication of strong heteromolecular interaction in liquid mixtures and is attributed to charge transfer, dipole-dipole, dipole-induced-dipole interaction and hydrogen bonding between unlike components, while a positive sign indicates a weak interaction and is attributed to dispersion forces (London forces) [8, 9]. Compared to water molecule, the size of the pyridine molecule is large having a ring structure. At low molefractions of pyridine, both these polar

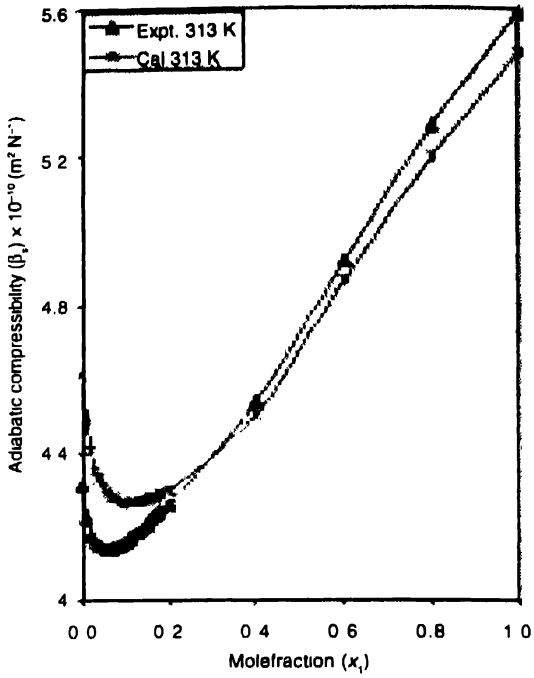

Figure 2(c). Variation of β_s^{Expt} and β_s^{cal} with molefraction (x_1) for the binary mixture pyridine + water at 313K.

molecules exhibit strong dipole attraction and forms a compact structure (*ie.* complex formation) with four water molecules and a pyridine molecule through hydrogen bonding. This results in the compressibility minimum at low molefractions of pyridine which inturn makes β_s^E to maximum negative. Further, the presence of maxima or minima or any abrupt change from the normal behaviour in the physical properties of a liquid mixture can be used as an indication of complex formation in it [10] Thus, the β_s minima at around 0.1, 0.085 and 0.06 molefractions of pyridine at 303, 308 and 313 K respectively show that there is formation of pyridine-water complexes at low concentrations of pyridine. The shift in β_s minimum towards lower concentration at higher temperature shows that the number of molecules forming complexes decrease with increase in temperature due to thermal randomization. Beyond x_1 = 0.28 molefraction of pyridine, the β_s^E values are found to be positive. This is because as the concentration of pyridine increases, the large pyridine molecule exhibits steric hindrance to the attractive dipole interactions which results in the disruption of the compact structure of the mixture and causes a positive excess value for β_s. Thus at low concentrations of pyridine, formation of pyridine-water complexes are effective whereas at higher concentrations its structure breaking property predominates.

Figure 3 shows the variation of β_s^{Expt} and β_s^{cal} as a function of concentration for the binary mixture PMMA + CB at two different temperatures 313 K and 323 K. The deviation

between experimental and calculated values of adiabatic compressibility remains almost same upto X = 0.75 at 313 K and thereafter shows a decreasing trend. But this decrease in trend starts even from lower concentration at 323 K. The decreasing trend can be seen upto 3% of solute PMMA concentration at both temperatures. The experimental curve crosses the theoretical curve at about X = 1 for both temperatures. It is clear from the figure that the deviation widens with increase in concentration at both temperatures. But at higher temperature, this widening increases very rapidly with increase in concentration. This shows the presence of interaction in the system

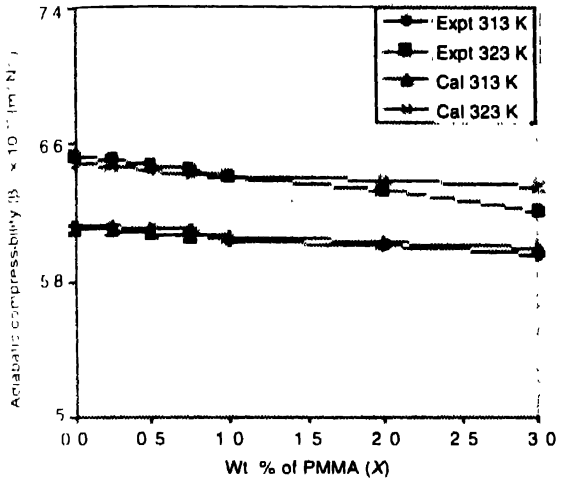

Figure 3 Variation of β_s^{Expt} and β_s^{cal} with Wt % of PMMA (X) for the binary mixture Polymethylmethacrylate + Chlorobenzene at 313 and 323 K

PMMA is a polymer which has bulky $COOCH_3$ groups and H_3 groups attached to alternate carbon atoms in the chain. At low concentrations of PMMA, only a few PMMA molecules interact weakly with chlorobenzene molecule resulting in small positive deviation of β_s. Even though the deviation is positive upto X = 0.95 at 313 K and up to X = 1 at 323 K, the deviation changes sign beyond the above concentrations. This is because as the concentration of PMMA increases, the number of PMMA molecules in the binary mixture also increases which results in direct interaction between PMMA molecules. Thus, it can be seen that though interaction between PMMA and CB molecules exists at low molefractions of PMMA, due to its large number and bulky size, direct interaction between PMMA molecules begins to dominate over PMMA and CB interaction. This causes a negative value for β_s^E at higher concentrations of PMMA. This result is in good agreement with that of Kalyanasundaram *et al* who studied this system using ultrasonic velocity [4].

The graph of pyridine-water system is taken with a scale different from that of the other two systems to get better clarity at lower concentration range.

5. Conclusion

An estimation of adiabatic compressibility of liquids at any higher temperature can be made using eq. [6] if its value at a lower temperature is known. The results show that the estimated values agree well with the experimental values for ideal mixtures such as benzene-toluene system. The deviation in β_s in a binary mixture may be due to the interaction between the molecules of the system.

References

[1] S Mohanan, V K Vaidyan and K V Kurian *Appl Phys. Lett* **70** 805 (1997)

[2] S Mohanan, V K Vaidyan and K V Kurian *Acustica, Acta Acustica* (W Germany), **83** 367 (1997)

[3] R G Bindu and S Mohanan *Proc Twelfth Kerala Science Congress* (Kerala, India) p.106 (2000)

[4] S Kalyanasundaram, A Manuel Stephan and A Gopalan *Indian J. Pure Appl. Phys* **34** 353 (June 1996)

[5] Gordon M Barrow *Physical Chemistry* (Tokyo : McGraw Hill, Kogakusha Ltd) p.280 (1979)

[6] P Babu, G Chandra Sekhar and N Prabhakara Rao *Indian J Pure Appl Phys* **38** 88 (2000)

[7] Peter P Betlow, Donald J Burton, Joseph E Routs *Introduction to the Chemistry of Life* (CBS College publishing, USA) 321 (1982)

[8] R J Fort and W R Moore *Trans. Faraday Soc* **61** 2102 (1965)

[9] Y Marcus *Introduction to Liquid State Chemistry*, (London . Wiley-Interscience) (1977)

[10] C S Adgaonkar, S N Jajoo and V S Deogaonkar *J. Acoust. Soc of India* **7** 75 (April 1979)